AN ENERGY DISPERSIVE X-RAY FLUORESCENCE STUDY OF SOME NEAR EASTERN OBSIDIANS

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Introduction

For over twenty five years the chemical sourcing of obsidian to study patterns of trade and exchange has been an important aspect of Near Eastern archaeology [Benedict et. al. 1980: Blackman 1984; Cann and Renfrew 1964; Cauvin et. al. 1986; Francaviglia 1990; Perlman and Yellin 1980; Renfrew, Dixon and Cann 1966, 1968; Wright 1969; Wright and Gordus 1969; Zarins 1990]. In a majority of these studies either neutron activation analysis or some form of atomic or optical spectroscopy was used to obtain the chemical composition of the obsidian. Both of these analytical methods can be costly and time consuming; also, in the case of spectroscopy, an actual sample of the material needs to be taken from the artifact.

One purpose of this paper is to illustrate the utility of energy dispersive x-ray fluorescence (EDXRF) in the characterization of obsidian from the Near East. This non-destructive method of analysis is low-cost, can be run quickly, and yields quantitative data. It should be stressed that EDXRF is not a new analytical technique, but one used extensively by archaeologists and geologists studying obsidian particularly in the Americas [Bouey 1991; Fowler et. al. 1989; Hughes 1984, 1988; Hughes and Smith 1993; Jack and Carmichael 1969; Shackley 1988, 1991, 1992].

Another purpose of this paper is to present some new chemical analyses of obsidian artifacts from three Near Eastern sites. The analyses performed on surface finds from Hamoukar and Hirbet Tueris in northeastern Syria and Umm Dabighiyah in Iraq (Figure 1).

X-Ray Fluorescence Spectrometry

The technique of x-ray fluorescence involves bombarding a material with an x-ray beam of known energy and wavelength. The primary x-ray beam displaces the electrons in the K, L, and M orbitals of the target atoms. The displaced electrons are then replaced by electrons from the outer orbitals of the target atoms; secondary or fluorescent x-rays are released as the outer orbital electrons loose energy to fill the inner orbitals. Each element in a material has a distinct secondary x-ray spectra. For the more interested reader, Williams [1987: 16–46] provides an in-depth overview of the physics of x-ray fluorescence.

After the secondary x-rays are produced, they can be collected and analyzed using one of two elemental methods. Energy dispersive x-ray fluorescence (EDXRF) machines utilize silicon based semi-conductors to detect and measure the intensity of the fluorescent x-rays [Hampel 1984: 21; Potts 1987: 286–303; Williams 1987: 110–120]. Wavelength dispersive x-ray fluorescence (WDXRF) machines utilize a crystal to diffract and separate the secondary x-rays to an x-ray detector. A comparison of the two methods are reviewed in Potts [1987: 299, 300] and Williams [1987: 100–120].

EDXRF is particularly well-suited for obsidian studies since it can accurately measure elements with atomic numbers 11 through 41 and some of the rare earth elements [Hampel 1984: 21, 22; Potts 1987: 312, 313]. The detection limit of EDXRF for niobium (Nb), rubidium (Rb), strontium (Sr), yttrium (Y), and zirconium (Zr), all trace elements used in sourcing obsidian (see below), is as low as 3.5 ppm to 6.0 ppm.

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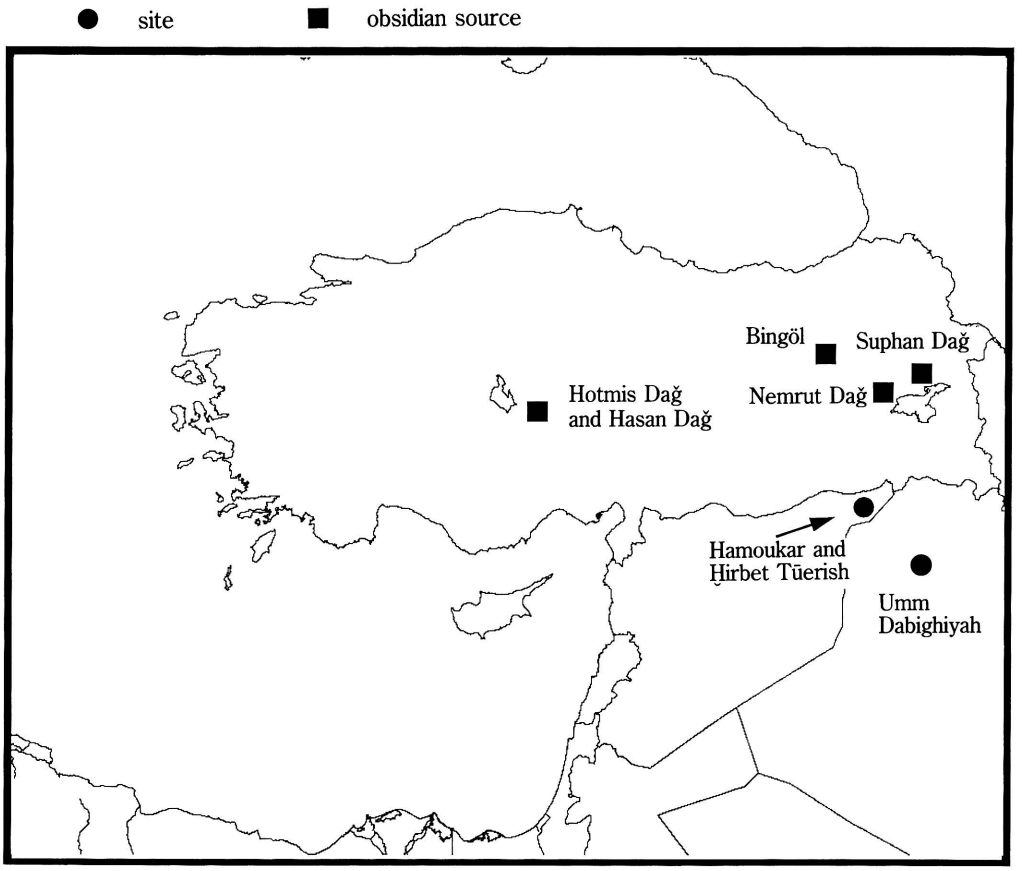

Fig. 1 Map of the sites and obsidian sources mentioned in the text

Methods of Analysis

The trace elements used to source obsidian in EDXRF and NAA studies are known as "incompatible elements" since they are incompatible with the solid-phase constituents in high temperature silicic melts and are most stable in the resulting glass phase [Cann 1983; Ferrara and Treuil 1975; Hess 1991; Mahood and Stimac 1990; Zielinski et. al. 1977]. They generally do not covary within a single silicic melt and their concentrations are unique for each volcanic event. The incompatible elements include niobium (Nb), rubidium (Rb), strontium (Sr), titanium (Ti), yttrium (Y), and zirconium (Zr). Other major and trace elements, such as chromium (Cr), cobalt (Co), iron (Fe), gallium (Ga), nickel (Ni), and sodium (Na), can vary extensively in a single obsidian source since they are easily absorbed into the solid phase within a silicic melt. Furthermore, iron and sodium can be lost due to hydration and secondary crystallization of the obsidian [MacDonald and Bailey 1973: N2].

The trace element analyses were performed in the Department of Geology and Geophysics, University of California, Berkeley, using a Spectrace^{TM} 440 [United Scientific Corporation] energy dispersive x-ray fluorescence spectrometer. The spectrometer is equipped with a rhodium x-ray tube, a 50 kV x-ray generator, and a Tracor X-ray (Spectrace^{TM}) TX 6100 x-ray analyzer using an IBM PC based microprocessor and Tracor reduction software. The x-ray tube was operated at 30 kV, 0.20 mA, using a .127 mm rhodium primary beam filter in an air path at 250 seconds livetime to generate x-ray intensity data. Secondary x-ray intensities were converted to concentration values by employing a least-squares calibration line established for each element from the analysis of up to 26 international rock standards certified by the U.S. Bureau of Standards, the U.S. Geological Survey, Canadian Centre for Mineral and Energy

Technology, the Centre de Recherches Pétrographiques et Géochimiques in France, and the Geological Survey of Japan.

To insure machine calibration, a known standard was run with the obsidian samples. Table IA shows a comparison between values recommended for RGM-1, a U.S. Geological Survey rhyolite rock standard, and the results obtained for it from this study. This data indicates that the machine accuracy is quite high. The maximum amount of error in each elemental reading is listed in Table IB.

Artifact Analyses

The obsidian artifacts in this study came from Hamoukar (Hamukar) and Hirbet Tueris in northeastern Syria and Umm Dabighiyah in Iraq [see Figure 1]. Both Hamoukar and Hirbet Tueris are unexcavated tells in the Habur River basin east of the al-Radd marsh and close to the border with Iraq [Dobel 1978: 103, 108, 194–197; van Liere 1963]. Hamukar is believed by van Liere [1963: 114–120] to be the capital of the Mitanni state, Wassukanni. Hirbet Tueris is a smaller tell near Hamukar. From surface finds of pottery, occupation continued at Hirbet Tueris through the second millennium BC [Dobel 1978: 103]. Umm Dabighiyah is a small tell located in the dry steppe zone of the Jazira. Excavations were conducted there in the early 1970s [Kirkbride 1972, 1973a, 1973b]. The finds indicate that the site was occupied during the sixth millennium BC.

The artifacts collected from Hamukar (Nos. 14511–14518, 14520, 14521) and Hirbet Tueris (Nos. 14105–14115) are retouched blades ranging in length from 1.5 cm to 6.0 cm. Blades 14511 and 14514 both contain cortex on one side. The artifacts from Umm Dabighiyah consist of two small re-touched flakes and a piece of debitage.

Table II contains the concentration (in ppm) of the incompatible elements analyzed by EDXRF for this study. Table III contains the concentration of the minor and trace elements in the artifacts. To see how many obsidian sources are present, selected incompatible elements are plotted against each other in Figures 2 through 5. Figure 2 is a plot of Sr versus Zr, Figure 3 is a plot of Y versus Zr, and Figure 4 is a plot of Nb versus Rb, and Figure 5 is a plot of Sr versus Y.

In all four graphs it is clear that the obsidian used at these sites came from three distinct sources.

Table IA

Sample	Ti	Mn	Fe	Rb	Sr	Y	Zr	Nb
RGM-1 (Govindaraju 1989)	1600	279	12998	149	108	25	219	8.9
RGM-1 (this study)	1514.29 +/−108	234.72 +/−28	13631.28 +/−457	147.43 +/−2	106.14 +/−4	23.5 +/−2	227.2 +/−5	8.87 +/−5

X-ray fluorescence concentrations for selected trace elements of RGM-1. The +/− values represent the first standard deviation computations for the group of measurements. All values are in parts per million (ppm) as reported in Govindaraju (1989) and this study. RGM-1 is a U.S. Geological Survey rhyolite (obsidian) rock standard.

Table IB

Element	Error (+/−)	Element	Error (+/−)
Nb	5.0 ppm	Fe	.05%
Rb	3.5 ppm	Mn	35 ppm
Sr	5.5 ppm	Ti	118 ppm
Y	3.0 ppm	Zn	7 ppm
Zr	7.5 ppm		

Listed above are the maximum amount of measurement errors for each elemental concentration listed in Table II and Table III.

Table II

Sample number	Nb	Rb	Sr	Th	Y	Zr
14511	53.8	220.9	7.5	17.6	119.4	1185.1
14512	34.8	200.5	21.7	23.6	50.6	266.3
14513	68.3	241.5	7.3	31.3	129.9	1263.0
14514	65.2	239.8	7.2	32.8	134.9	1254.1
14515	63.7	225.7	4.9	27.6	123.2	1193.6
14516	58.0	222.8	6.7	29.6	119.1	1148.3
14517	61.7	238.3	5.3	29.7	127.7	1253.3
14518	62.0	218.9	7.0	25.8	124.0	1180.9
14520	65.9	236.0	4.4	27.9	122.6	1240.2
14521	64.3	232.5	5.0	25.8	124.0	1226.5
145105	60.0	221.8	13.5	32.9	124.8	1190.5
145106	58.2	229.3	6.4	29.1	127.2	1208.5
145107	63.6	219.7	5.5	25.8	125.1	1179.4
145108	58.9	212.0	8.9	31.4	117.5	1155.3
145109	63.9	230.7	12.8	30.2	123.6	1204.2
145110	60.6	232.4	9.0	32.9	125.3	1214.9
145111	57.0	228.1	8.9	31.1	121.2	1165.3
145112	56.9	229.8	7.2	23.4	123.6	1206.8
145113	63.2	229.4	5.5	26.8	126.2	1226.6
145114	65.4	232.0	6.0	32.4	127.0	1223.5
145115	62.8	235.5	6.3	27.8	124.7	1228.6
UD1	55.6	220.3	4.1	40.0	124.5	1122.7
UD2	13.9	223.2	51.7	31.6	30.1	297.7
UD3	62.4	204.5	5.4	37.2	122.5	1086.3

Concentration of incompatible and trace elements in the artifacts from Hamakar (Nos. 14511 to 14518, 14520, 14521), Ḫirbet Tūeris (Nos. 14105 to 14115), and Umm Dabighiyah (Nos. UD1 to UD3). All concentrations are listed in parts per million (ppm).

Table III

Sample number	Fe (%)	Mn	Ti	Zn
14511	2.08	393.9	900.4	174.8
14512	1.18	466.8	652.0	92.4
14513	2.49	526.7	993.1	192.4
14514	2.60	511.3	1126.2	197.5
14515	2.20	458.7	950.8	175.7
14516	2.34	429.3	929.6	201.2
14517	2.44	491.3	1039.1	193.7
14518	2.28	434.4	941.4	183.1
14520	2.39	484.1	991.9	188.7
14521	2.37	525.8	1001.9	186.9
145105	2.14	421.2	991.5	169.6
145106	2.50	492.0	960.4	202.2
145107	2.23	413.1	918.5	186.6
145108	2.15	413.5	906.7	190.2
145109	2.24	450.2	967.8	179.5
145110	2.32	451.1	1013.4	181.2
145111	2.36	464.9	1108.6	209.5
145112	2.34	452.8	994.8	202.8
145113	2.37	462.7	1064.2	190.5
145114	2.30	524.3	1062.9	193.0
145115	2.30	459.4	883.8	179.4
UD1	3.38	572.7	2065.9	220.1
UD2	1.53	266.7	1359.4	65.7
UD3	2.02	334.6	973.0	174.1

Concentration of minor and trace elements in the artifacts from Hamakar (Nos. 14511 to 14518, 14520, 14521), Ḫirbet Tūeris (Nos. 14105 to 14115), and Umm Dabighiyah (Nos. UD1 to UD3). All concentrations, except iron (Fe) are listed in parts per million (ppm). The iron concentration is in %.

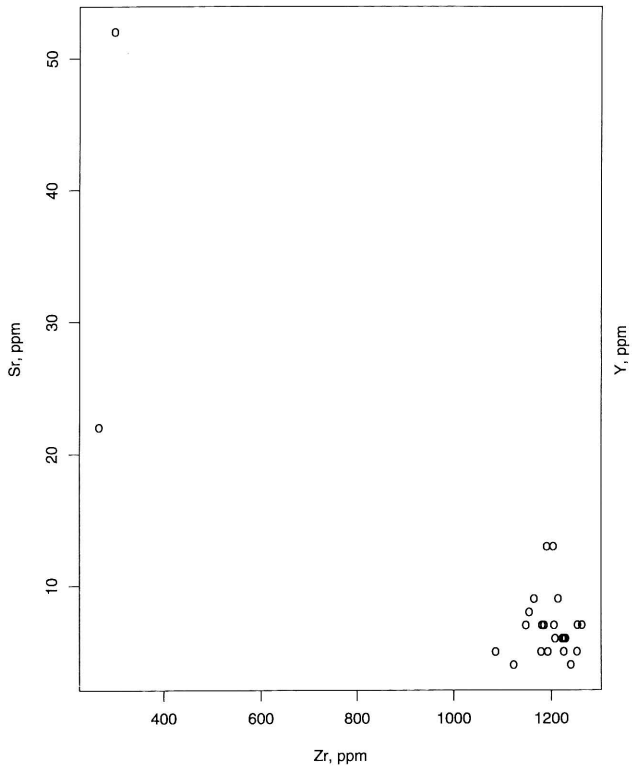

Fig. 2 Plot of Sr concentration versus Zr concentration

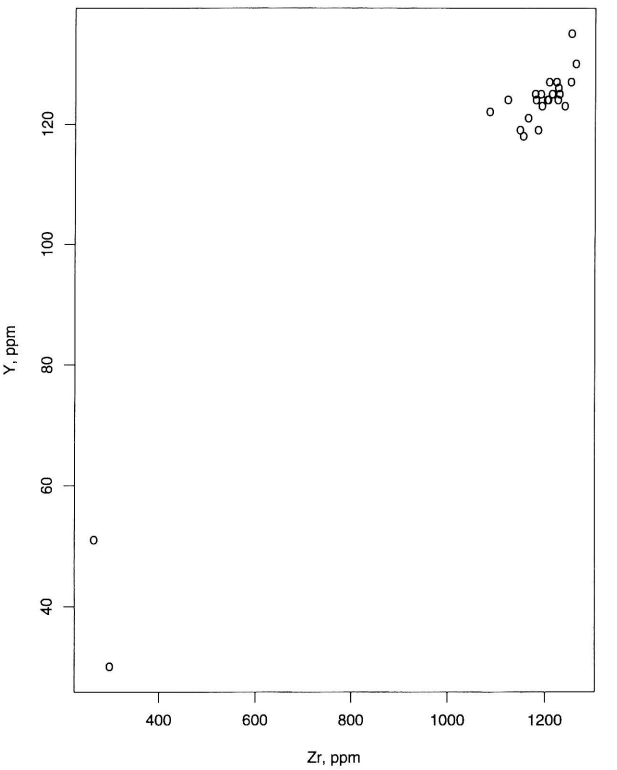

Fig. 3 Plot of Y concentration versus Zr concentration

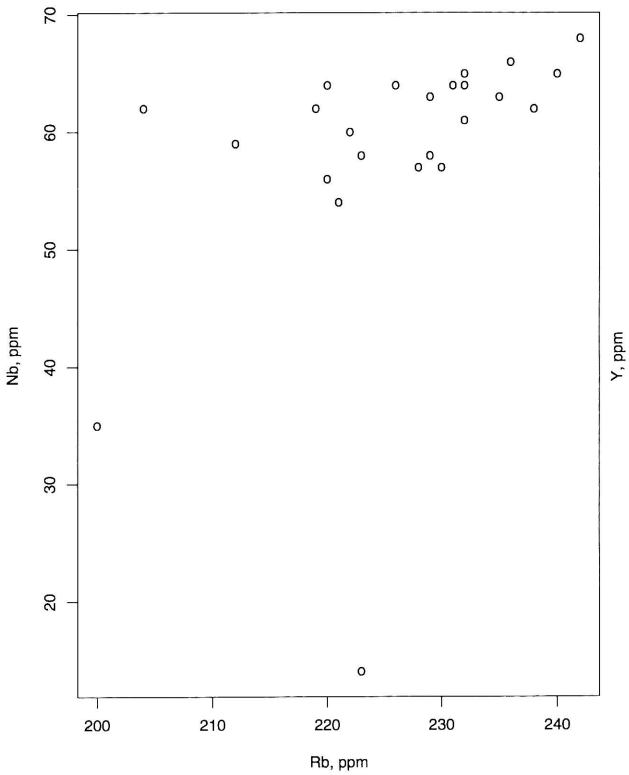

Fig. 4 Plot of Nb concentration versus Rb concentration

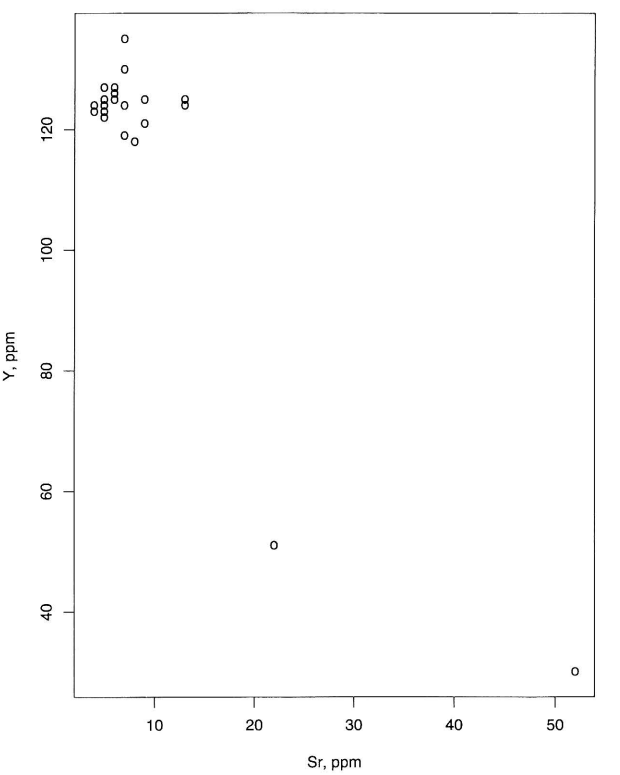

Fig. 5 Plot of Y concentration versus Sr concentration

Twenty-two out of 24 artifacts came from a single source; the remaining two artifacts each came from a distinct source.

These sources can be identified by using the published data in Benedict et. al. [1980], Blackman [1984: 42–49] and Cauvin et. al. [1986: 92]. On the basis of the iron, rubidium, thorium, and zinc concentrations, the majority of the artifacts are made from obsidian coming from one of the Nemrut Dag sources. Due to the lack of data on two of the obsidian flows at Nemrut Dag, it cannot be ascertained which of the four sources provided the obsidian. On the basis of the iron, manganese, strontium, titanium, yttrium, zinc and zirconium concentrations, sample UD2, the debitage from Umm Dabighiyah, is made from obsidian coming from source B at Bingöl, Turkey. Blade 14512 from Hamukar was made of obsidian from an unknown source. Its composition is similiar to obsidian artifacts found at Zarnaki Tepe north of Lake Van [Blackman 1984: 48–49].

Discussion

As can be expected, the obsidian used by these three sites came from eastern Turkey. Past research [Blackman 1984: 34–36; Renfrew, Dixon and Cann 1966: 40–49] has shown that most of the obsidian used in Mesopotamia and the Iranian highlands during the 8th millennium BC through the mid-3rd millennium BC came from Nemrut Dag. The Bingöl sources and the source supplying Zarnaki Tepe were subsidiary to Nemrut Dag at this time. After the 3rd millenium BC, Nemrut Dag lost its promenience in the Iranian highlands and other sources began to be used there. It is uncertain what obsidian sources were in use in Mesopotamia from the mid-3rd millenium BC onwards.

Previous sourcing work on the obsidian from Umm Dabighiyah used color only [Kirkbride 1972: 11; Mellart 1975: 138]. On the basis of color, it was determined that the obsidian came from the Lake Van area. The EDXRF analyses provide more specific information, indicating that the osbsidian came from a source at Nemrut Dag and Bingöl source B.

The analyses of the obsidian from Hamoukar and Hirbet Tueris suggest that Nemrut Dag could have been a major source of obsidian as late as the 3rd and 2nd millennium BC for the inhabitants of the Habur River basin. Lake Van was just outside the boundary of the Mitanni province of Alshe [Roaf 1990: 134]. It is quite possible that the Mitanni had ready access to the obsidian at Nemrut Dag, but more research is needed on this issue.

The presence of cortex on two of the blades from Hamoukar and Hirbet Tueris and the debitage from Umm Dabighiyah needs to be noted. These two features suggest that the obsidian nodules were traded rather than the finished tools.

Conclusion

Over 90% of the obsidian artifacts analyzed were made from obsidian procured from Nemrut Dag. The remainder of the artifacts were made of obsidian from Bingöl and an unknown source.

Even though obsidian sourcing studies have been undertaken for nearly thirty years, research still remains to be done in three major areas. First, the unknown obsidian sources need to be located and characterized. More intensive chemical studies need to be done on obsidain from Hotmis Dag, Lake Sevan, Nemrut Dag, and Suphan Dag. Finally, there needs to be more analyses of obsidain from 3rd and 2nd millennium sites in Mesopotamia. In all of these areas EDXRF can be an effective analytical tool in the investigation of Near Eastern archaeological obsidian.

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